Fate of 2-Chloro Ethyl Ethyl Sulfide on 13X Molecular Sieve Adsorbent

Implications for Regenerative Filtration

2003 Joint Scientific Conference on Chemical & Biological Defense Research

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Introduction

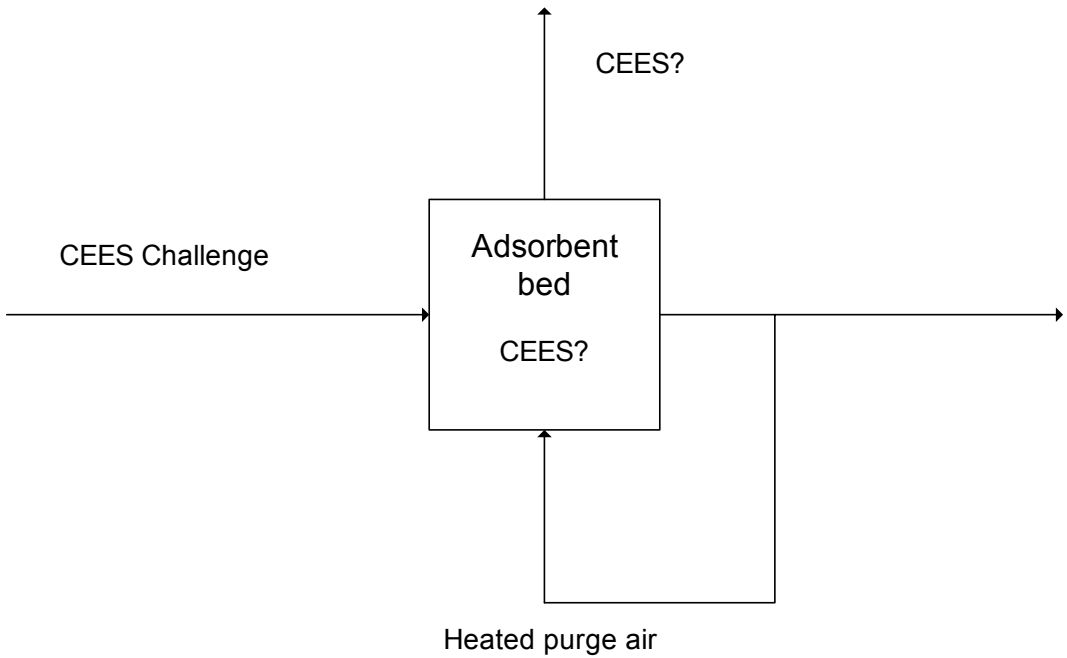
- Regenerative filtration technology offers the promise of greater capacity and breadth of chemical protection than the currently fielded single pass filtration technology.

- Many past and current regenerative filtration prototypes utilize zeolite adsorbents such as 13X molecular sieve.

- The current carbon based adsorbent knowledge base must be expanded to include adsorbate-adsorbent interaction under regenerative filtration conditions.

Objective

- Evaluate the behavior of 2-chloro ethyl ethyl sulfide (CEES), a mustard (HD) simulant, on 13X molecular sieve under thermal regeneration conditions.



Approach

- Expose a packed bed of 13X to a vapor challenge of CEES until it reaches saturation.
- Purge the saturated bed with reverse flow and introduce step-wise heating.
- Evaluate at conditions relevant to regenerative filtration.
  - Examine effect of preloaded water.
  - High face velocity (several times that of M48).
  - Restrained adsorbent bed.

Experimental

Preparation of 13X adsorbent

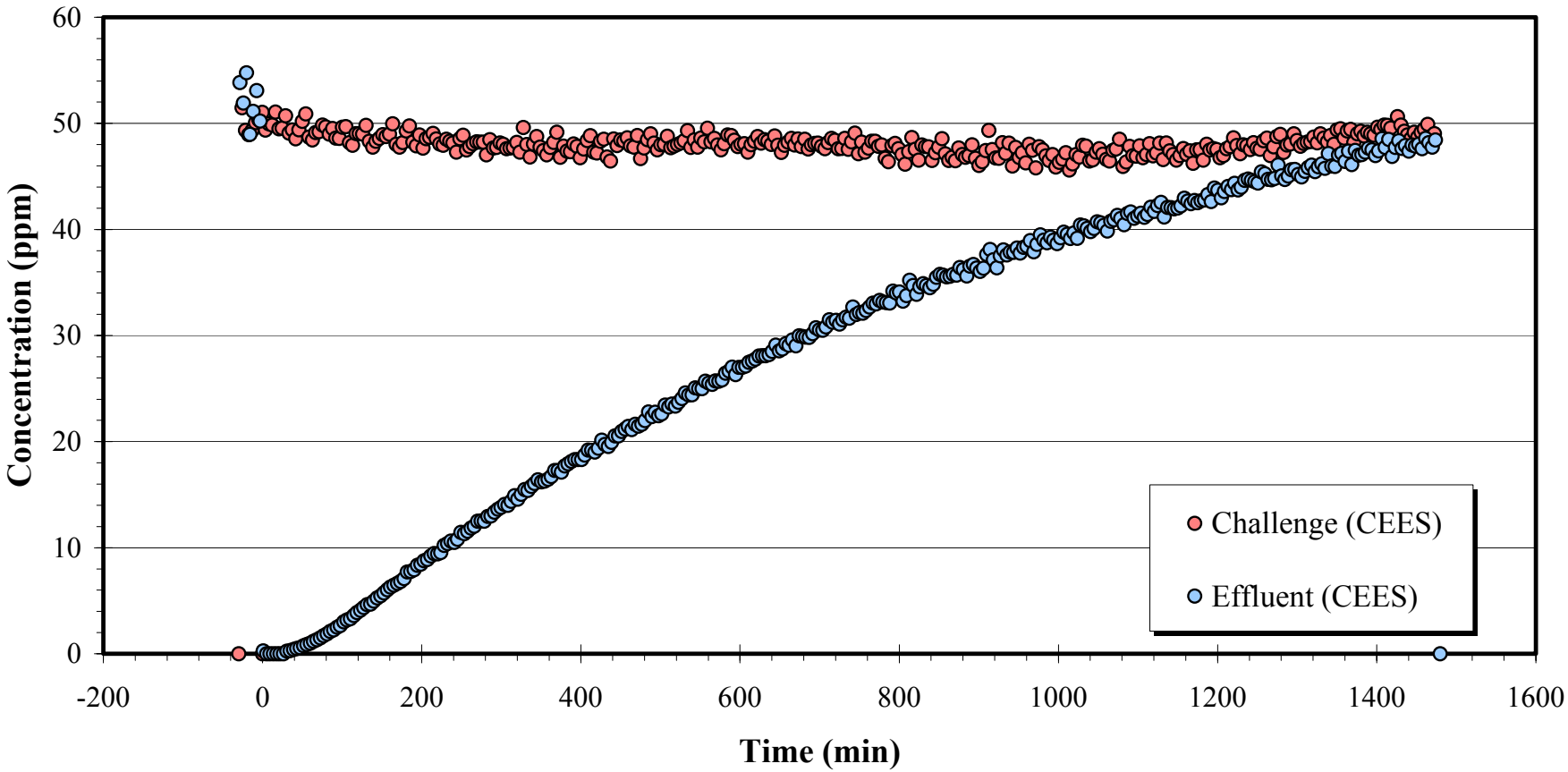
CEES feed concentration	200 mg/m^3 (43 ppm)
Temperature	50 C
Bed depth	3 cm
Flow rate	50 LPM (21.1 C, 1 atm)
Face velocity	51.8 cm/s
Dew point	<-80 C to 0 C

Experimental

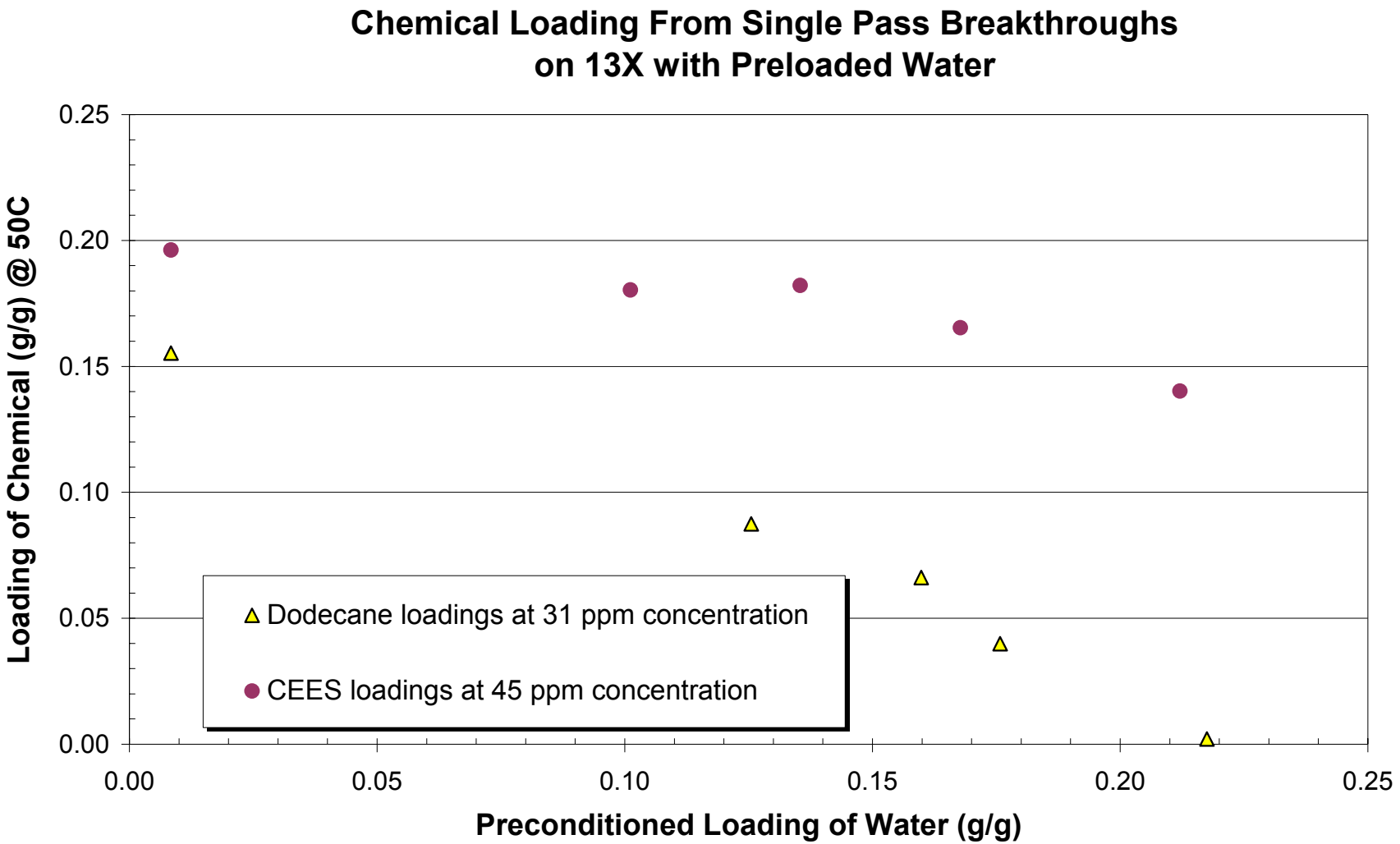
Purge of 13X adsorbent

Temperature	50 C to 125 C
Bed depth	3 cm
Flow rate	25 LPM (21.1 C, 1 atm)
Face velocity	25.8 cm/s @ 50 C
Dew point	<-80 C

Results


Breakthrough of CEES on 13X Adsorbent
43 ppm CEES challenge, 51.8 cm/s velocity, 3 cm bed depth, <-80 C dew point
Concentration (ppm)
60
50
40
30
20
10
0
-200
0
200
400
600
800
1000
1200
1400
1600
Time (min)
Challenge (CEES)
Effluent (CEES)

Results


Chemical Loading From Single Pass Breakthroughs
on 13X with Preloaded Water
Loading of Chemical (g/g) @ 50C
0.25
0.20
0.15
0.10
0.05
0.00
0.00
0.05
0.10
0.15
0.20
0.25
Preconditioned Loading of Water (g/g)
Dodecane loadings at 31 ppm concentration
CEES loadings at 45 ppm concentration

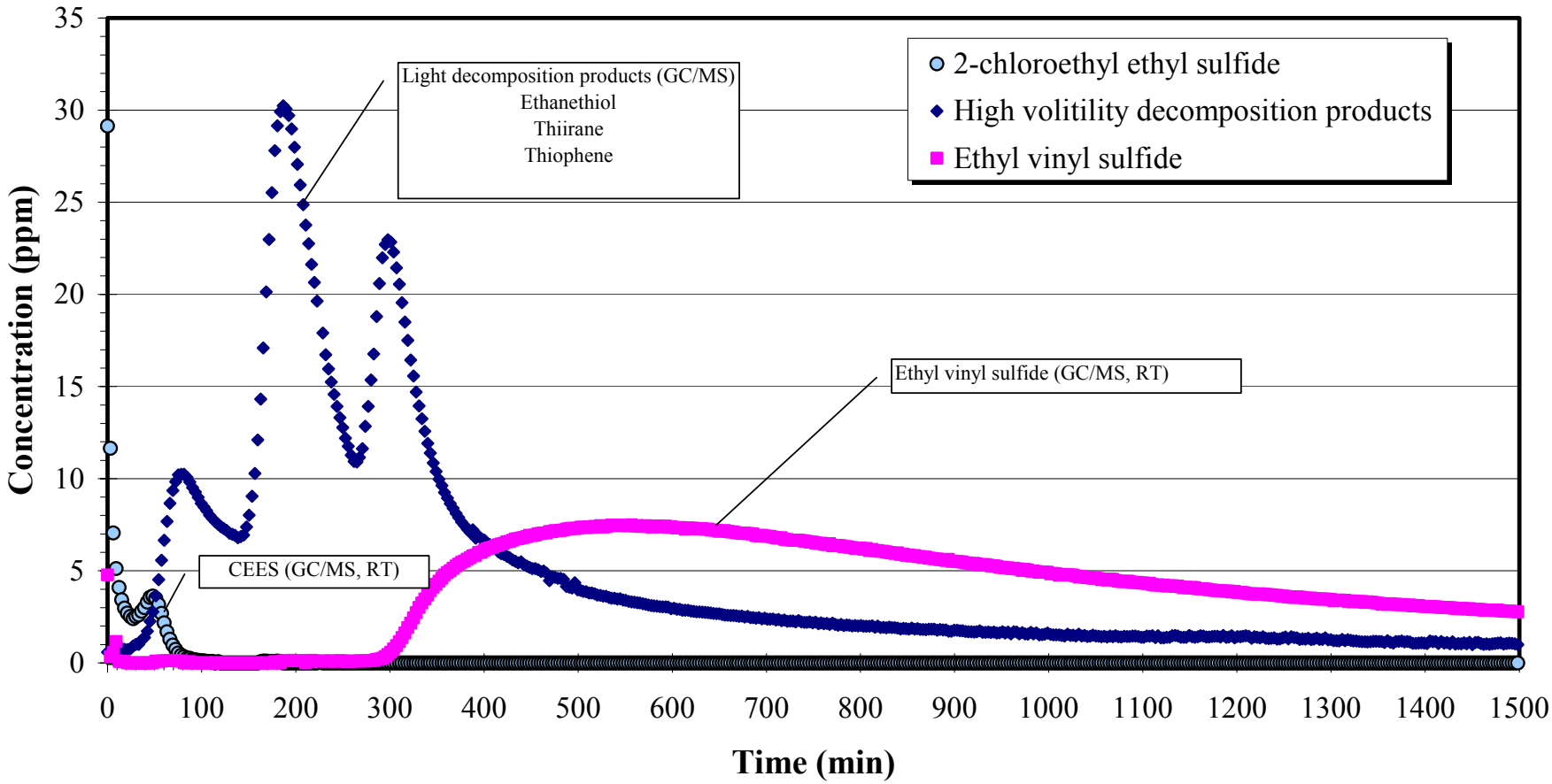
Results

- Identification of purge components
  - Sample 1
    - GC FID
      - One low retention time peak, no other detectable peaks
    - GC/MS suggests presence of following compounds
      - Ethanethiol
      - Thiirane
      - Thiophene
      - Diethyl sulfide
      - Diethyl disulfide (oxidation product of ethanethiol)
      - CEES
  - Sample 2
    - GC FID
      - CEES peak and two unidentified peaks
    - GC/MS suggests presence of following compounds
      - Ethyl vinyl sulfide
      - CEES
    - Confirmed presence of ethyl vinyl sulfide by matching retention time and response with standard.

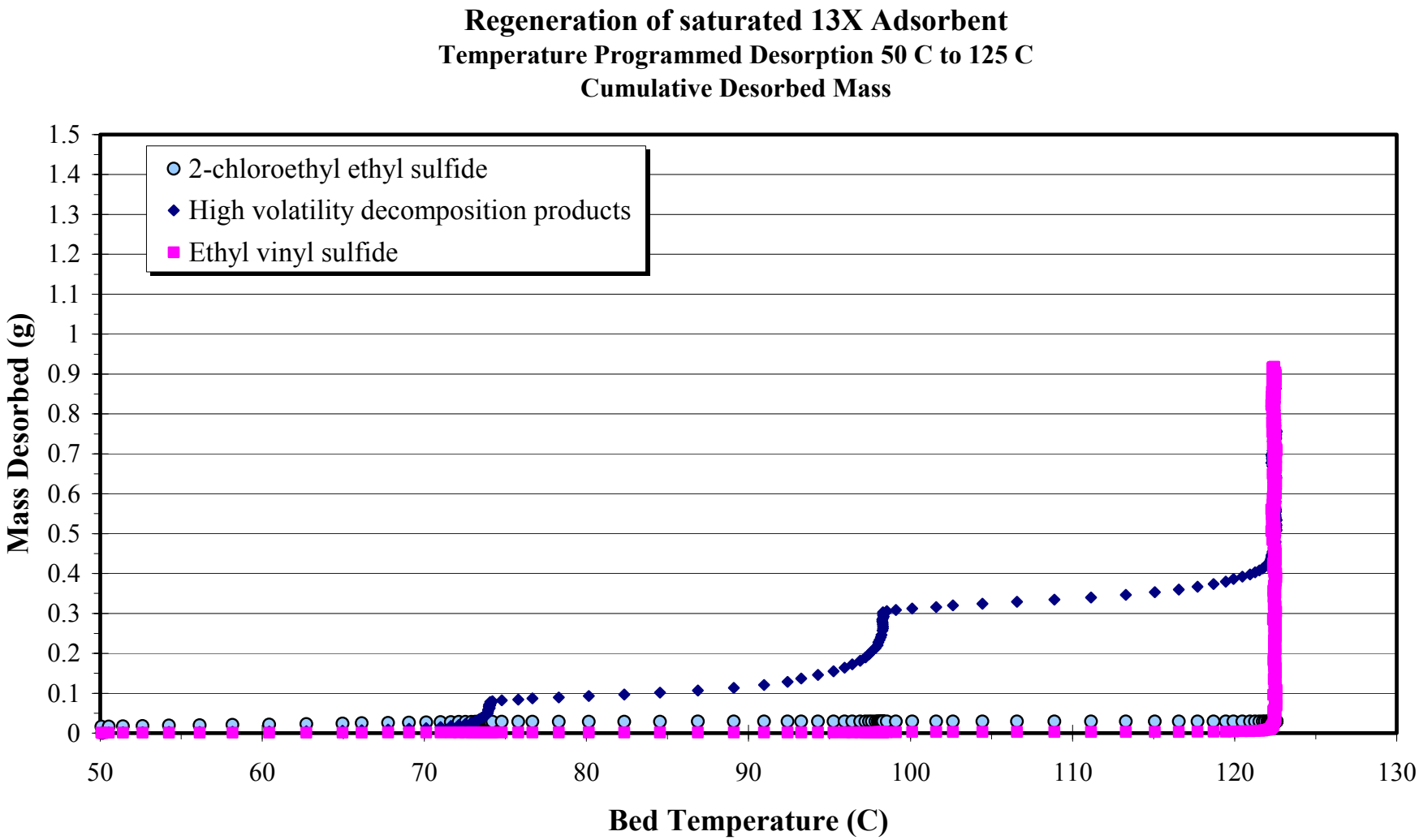
Results

Regeneration of saturated 13X adsorbent

Temperature Programmed Desorption 50 to 125 C



Results

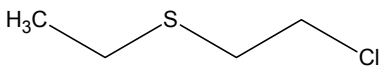

Regeneration of saturated 13X Adsorbent
Temperature Programmed Desorption 50 C to 125 C
Cumulative Desorbed Mass
2-chloroethyl ethyl sulfide
High volatility decomposition products
Ethyl vinyl sulfide
Mass Desorbed (g)
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
60
70
80
90
100
110
120
130
Bed Temperature (C)

Results

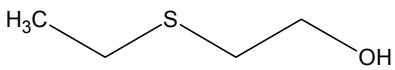
Mass balance

Dew Point	Mass loaded (g)	CEES recovered (g)	Reaction products (g)	Total recovery (%)	Mass balance (%)
< -80 C	7.40	0.04	2.59	36	99
-40 C	6.81	0.06	2.01	31	100
-20 C	6.24	0.03	2.37	38	101

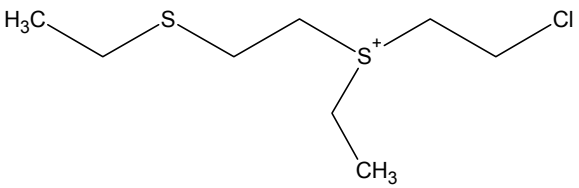
Results



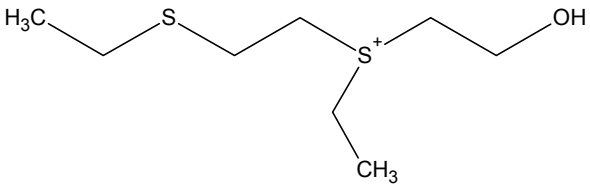
2-chloroethyl ethyl sulfide



HCl H_2O



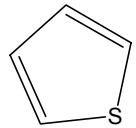
(2-chloroethyl)(ethyl)[2-(ethylthio)ethyl]sulfonium



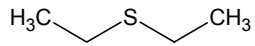
ethyl[2-(ethylthio)ethyl](2-hydroxyethyl)sulfonium

CEES and potential hydrolysis products

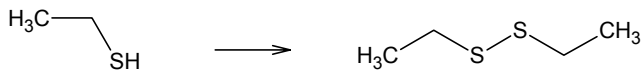
thiirane



thiophene



diethyl sulfide

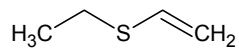


ethanethiol

diethyl disulfide

Maximum generation 95-120 C

Maximum generation 122 C



ethyl vinyl sulfide

Decomposition products

Summary

- One decomposition product identified: ethyl vinyl sulfide.
  - Requires a 122 C bed temperature for desorption.
  - Purges at long times with first order kinetics.
- Several other possible desorption products suggested by data.
  - GC FID method does not allow resolution of 0.64 min RT peak.
  - Possible products are fragments or cyclic derivatives of CEES.
  - Temperature at which the desorption concentration peaks, rises with increased preloaded water (95-120 C).
  - Purges at long times with second order kinetics.

Conclusions

- CEES undergoes hydrolysis and decomposition under conditions relevant to regenerative filtration on 13X adsorbent.
- Less than 1% of loaded CEES is purged as CEES, which is <2% of the total purge mass.
- 13X adsorbent is not fully regenerated when tested with CEES under the test conditions (<50%).
- Future work
  - Test mustard under similar conditions.
    - Literature suggests mustard may be less reactive but produce analogous (mustard chemistry) decomposition products.
  - Design apparatus for screening desorption properties (reactivity, dynamics, equilibrium) for regenerative filtration adsorbent candidates under a wide variety of conditions. This would be an important engineering tool for regenerative filtration system design.

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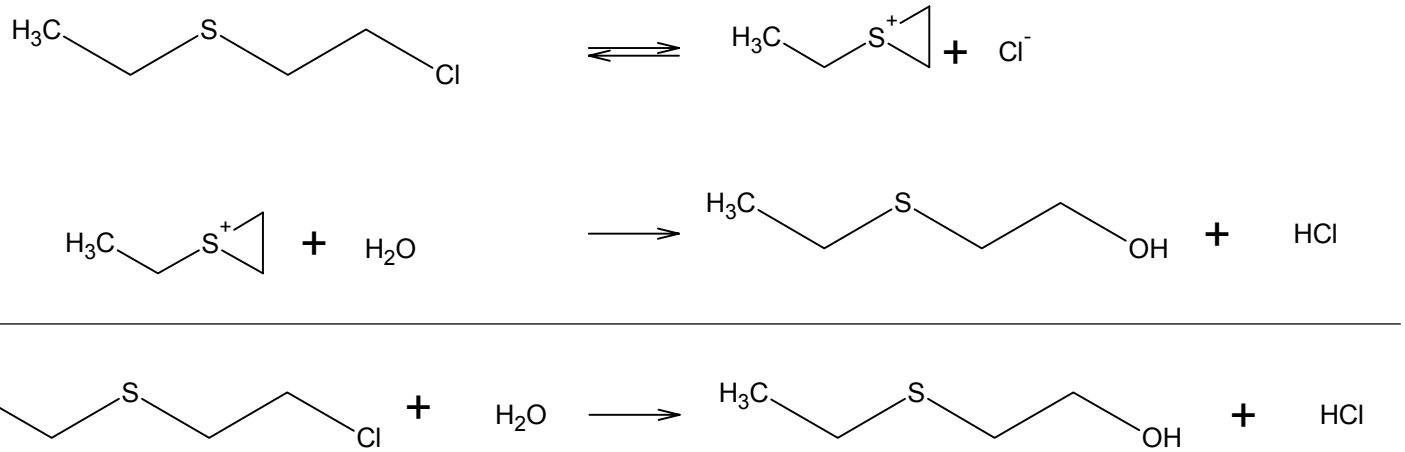
- Guild Associates, Inc.
  - Roy Brown
  - James Kotary
- Geo-Centers, Inc.
  - Kathy Matson

Background

- Hydrolysis of 2-chloroethyl ethyl sulfide in solution*

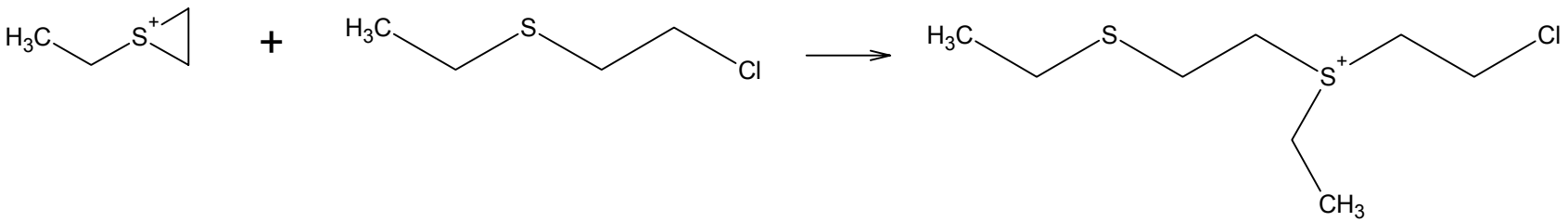


  - First order kinetics dominate when CEES is infinitely dilute.
  - Major hydrolysis products are HEES and HCl.

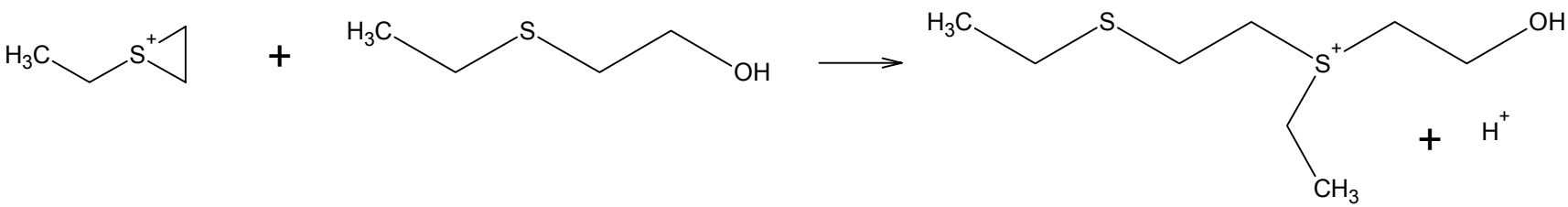
* Yang, Y., et al., "Mechanisms of Interactions of 2-chloroethyl sulfides with Water.", CRDEC-SP-88013, Nov 1987

Background

- Hydrolysis of 2-chloroethyl ethyl sulfide in solution.
  - For higher concentrations of CEES, reaction proceeds to equilibrium of CEES, HEES, and EHT.



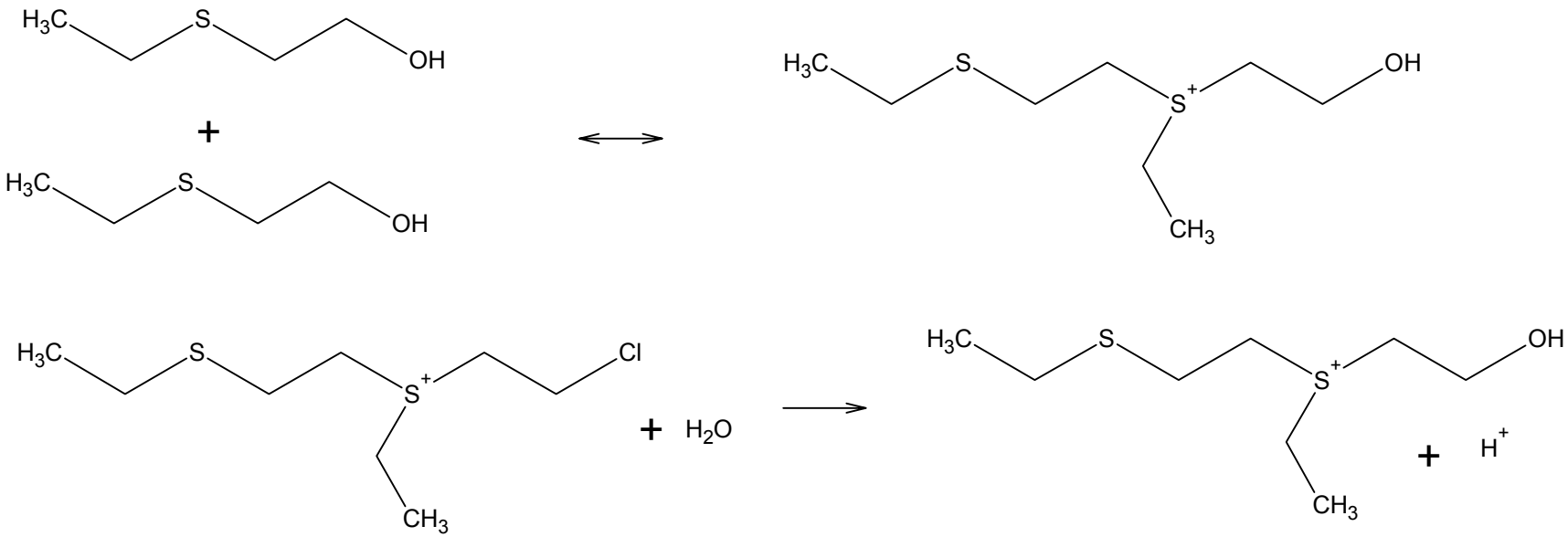
(2-chloroethyl)(ethyl)[2-(ethylthio)ethyl]sulfonium



ethyl[2-(ethylthio)ethyl](2-hydroxyethyl)sulfonium

Background

- Hydrolysis of 2-chloroethyl ethyl sulfide in solution.
  - For higher concentrations of CEES, reaction proceeds to equilibrium of CEES, HEES, and EHT.



Background

	CEES $CH_3CH_2SCH_2CH_2Cl$	**Mustard** $S(CH_2CH_2Cl)_2$
Molecular weight	124.6	159.1
Boiling point	157.1 C	227.8 C
Specific gravity	1.07 @ 25 C	1.27 @ 20 C
Water solubility*	$4.85 * 10^{-2}$ M	$4.44 * 10^{-3}$ M
Hydrolysis products	HCl, HEES, EHT, sulfonium salts	HCl, CH, TG, sulfonium salts

* Yang, Y. et al., "Solubility Properties and Rates of Solution of Mustard Gas and 2-Chloroethyl ethyl sulfide", CRDEC-TR-88043, February 1988

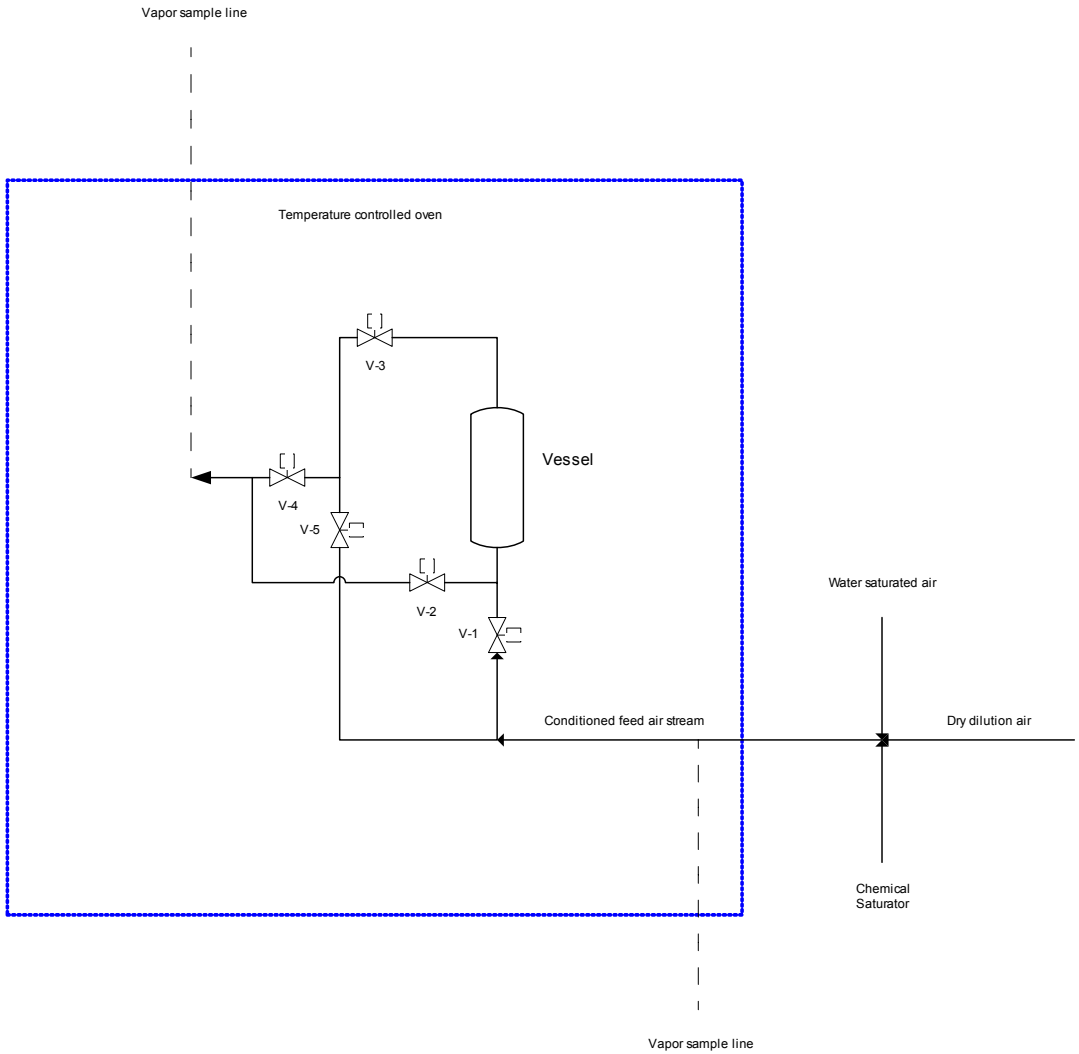
Background

- Behavior of neat HD on NaY (13X)* [room temp]
  - HD + H_2O → CH + TG → CH-TG
- Thermal desorption of HD from CSC carbon**
  - Combination of hydrolysis and thermal decomposition
  - Decomposition products 1,2 dichloroethane, 2-chloroethanol, 1,4 thioxane, 1,4 dithiane, sulfides, ethers
  - Only low level concentrations examined.

* Wagner, G.W., Bartram, P. W., "Reactions of VX, HD, and Their Simulants with NaY and AgY Zeolites. Desulfurization of VX on AgY.", Langmuir. 1999, 15, 8113-8118

** Karwacki, C. J., et al., "Effect of Temperature on the Desorption and Decomposition of HD from Activated Carbon.", ERDEC-TR-555, Dec 1998.

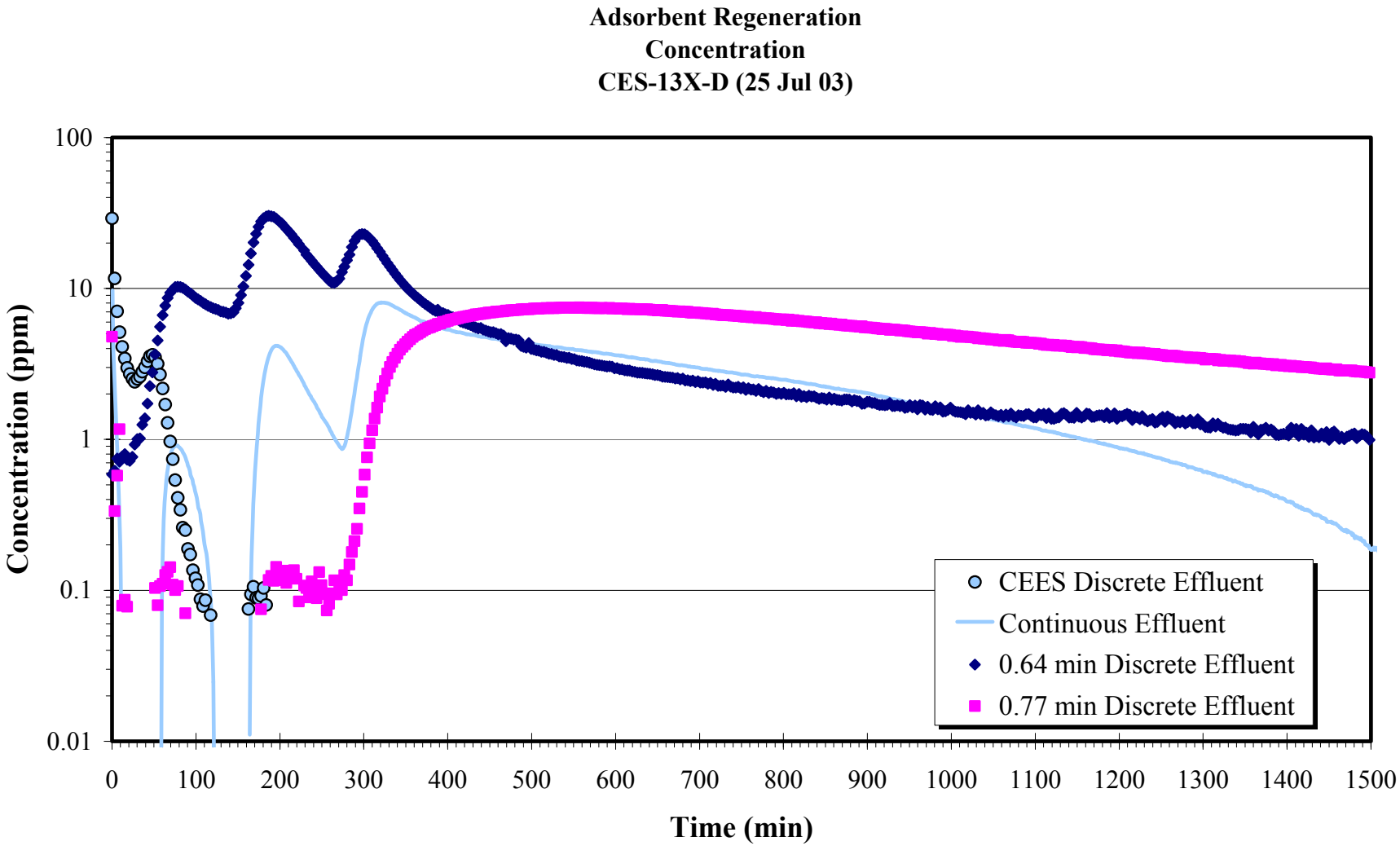
Experimental



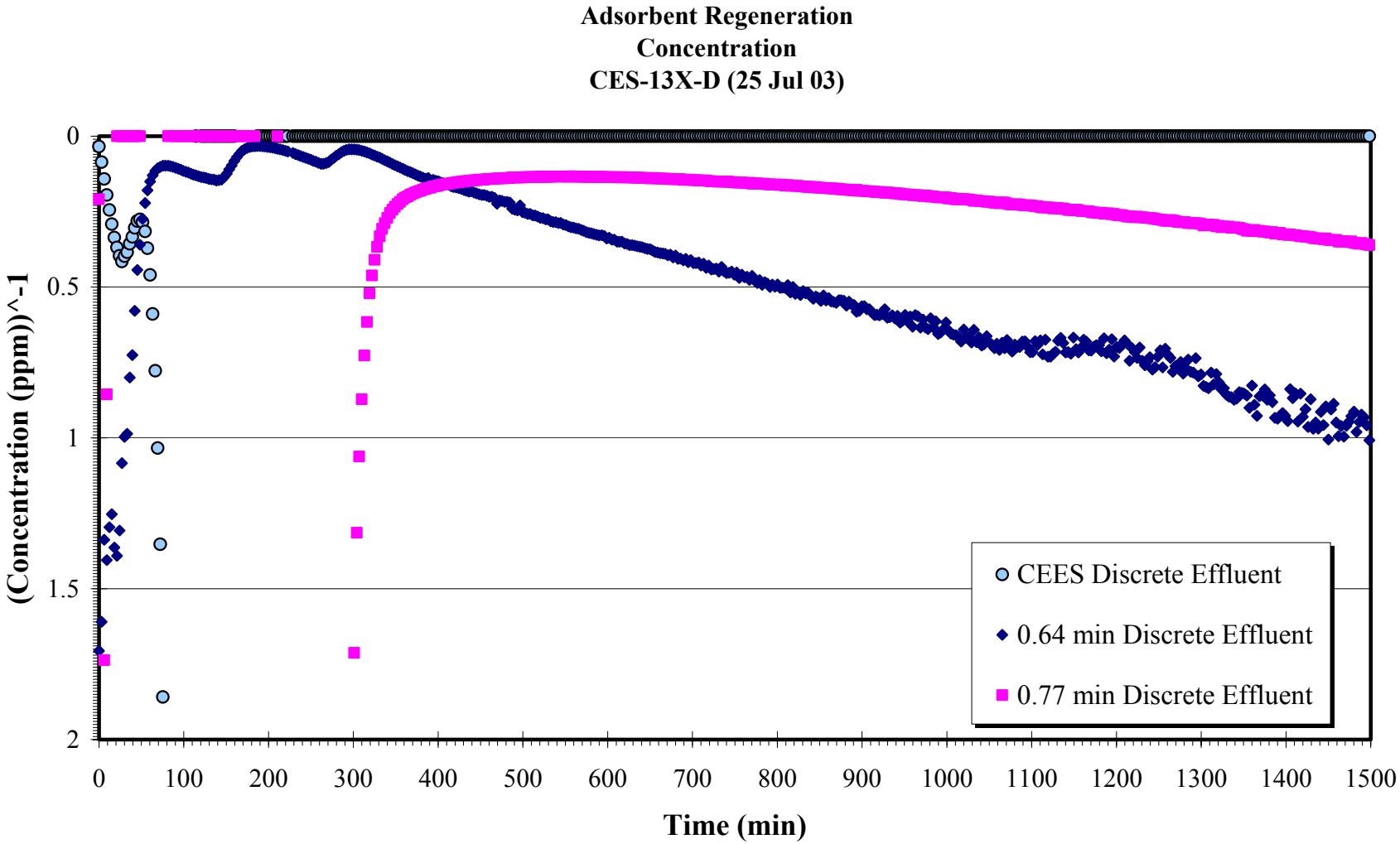
Experimental

- Analytical equipment.
  - Preparation and purge of adsorbent bed.
    - Continuous feed and effluent signal.
      - Direct FID voltage output.
    - Discrete feed and effluent signal.
      - GC fid, 110 c.
      - HP-1701 column (14%-cyanopropyl-phenyl)-methylpolysiloxane).
  - Sampling of bagged purge effluent.
    - Transfer at 25 C at 500 ml/min on Tenax.
    - Desorb contents to GC/MS with FID detector.

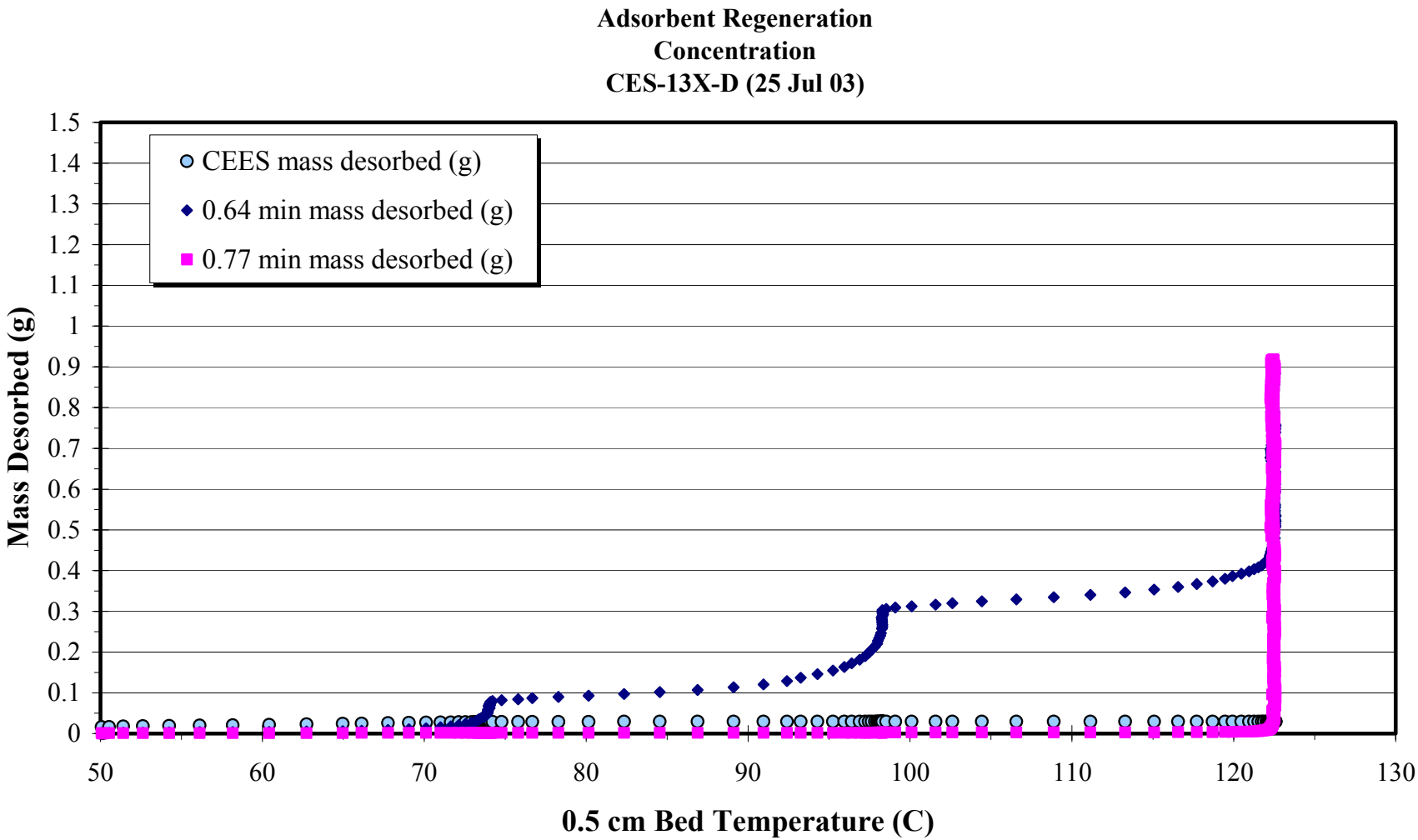
Results


Adsorbent Regeneration
Concentration
CES-13X-D (25 Jul 03)
Concentration (ppm)
100
10
1
0.1
0.01
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
Time (min)
CEES Discrete Effluent
Continuous Effluent
0.64 min Discrete Effluent
0.77 min Discrete Effluent

Results


Adsorbent Regeneration
Concentration
CES-13X-D (25 Jul 03)
(Concentration (ppm))^-1
0
0.5
1
1.5
2
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
Time (min)
CEES Discrete Effluent
0.64 min Discrete Effluent
0.77 min Discrete Effluent

Results


Adsorbent Regeneration
Concentration
CES-13X-D (25 Jul 03)
CEES mass desorbed (g)
0.64 min mass desorbed (g)
0.77 min mass desorbed (g)
Mass Desorbed (g)
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
60
70
80
90
100
110
120
130
0.5 cm Bed Temperature (C)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